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THE SOLUTION OF GOLD IN THE SURFACE ALTERATIONS OF ORE BODIES

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The leaching of gold from the outcrop of auriferous lodes has been the subject of much discussion, and many contradictory statements regarding the chemistry involved have arisen in the literature. Frequently these statements are based on experimental evidence, and the contradictions may be explained, in part at least, by a lack of uniformity in the conditions under which the experiments were carried out, and a tendency to ignore the conditions of temperature and concentration of solution that we are justified in supposing to be operative in the surface alteration of such deposits.

Clarke¹ has summarized the natural solvents for gold as reported by various observers. Their experiments, however, have been made under such a diversity of conditions that the results are not an adequate basis for comparisons, and it seemed desirable to ascertain where the emphasis should be placed in discussing this phase of the natural solution of gold.

At the suggestion of Professor W. H. Emmons, the writer undertook a series of experiments with a view of determining which of the various solvents noted are most effective in the solution of gold. By limiting the problem to alteration many substances are eliminated; only such as are known to occur in mine waters or in the gossan were studied, and the concentrations used are comparable to those shown by mine waters. The experiments were carried on at room temperature (18° to 25°), as Stokes² has shown that elevated temperatures have a very marked influence on the solubility of gold in ferric salt solutions.

A few of the solvents suggested by Don, Rickard, Lenher, and others were made the subject of a comparative study, the conditions of temperature and concentration being practically uniform for the

¹ Clarke, *U.S.G.S. Bull.* 330, 557.

² Stokes, *Econ. Geol.*, I, 650.

series. The substances studied were ferric sulphate, ferric chloride, sulphuric acid, hydrochloric acid, and manganese dioxide. These were covered by the following experiments, each in duplicate. Solution of gold is shown by loss of weight.

1. $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 + \text{Au}$
 (a) no weighable loss.
 (b) " " "
2. $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 + \text{MnO}_2 + \text{Au}$
 (a) no weighable loss.
 (b) .00017 g. loss.¹
3. $\text{FeCl}_3 + \text{HCl} + \text{Au}$
 (a) no weighable loss.
 (b) " " "
4. $\text{FeCl}_3 + \text{HCl} + \text{MnO}_2 + \text{Au}$
 (a) .01640 g. loss. Area of plate 383 sq. mm.
 (b) .01502 g. " " " " 348 " "

The solutions were tenth normal² with respect to ferric salt and to acid. In each duplicate 50 c.c. were used. In experiments 2 and 4, 1 g. of powdered manganese dioxide was added to each duplicate. The gold was obtained from Goldschmidt Bros. and assayed 99.9 per cent pure. It was rolled to a thickness of about .002 in., and cut into pieces of about 350 sq. mm. area, and one piece, weighing about 0.15 g., was used in each duplicate. The gold was washed with alcohol and ether and dried, then each piece was carefully weighed. The experiments were carried on in tightly stoppered test-tubes which were thoroughly shaken from time to time. After two weeks the pieces of gold were removed by means of a platinum wire, and washed with water, alcohol, and ether, in turn, before weighing. In experiments 2 and 4 a small amount of manganese dioxide adhering to the plates was removed by means of a solution of ferrous sulphate acidified with sulphuric acid, after which the plates were treated as above. At the end of two weeks all but experiment 4 gave negative results when weighings were made to 0.0001 g., and the balance was ex-

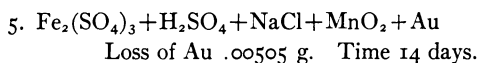
¹ This duplicate was found to contain a trace of Cl which probably accounts for the loss.

² Normal as used in this paper refers to "equivalent normal" solutions. Tenth normal concentration was selected rather arbitrarily except for the fact that it is well within the range of concentration shown by mine waters. (See table of analyses, p. 326.)

changed for one sensitive to 0.00001 g. which was used from that time on. The whole time was 34 days. In experiment 4 it will be seen that the losses in (a) and (b) are approximately proportional to the areas of the plates.

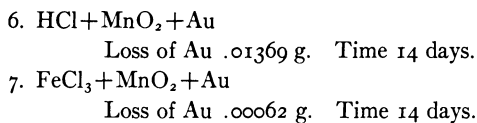
The results of these experiments, as given above, show conclusively that, of the conditions under consideration, the most favorable for the solution of gold involve the presence of manganese dioxide and chlorides. Although it is frequently stated that gold is readily soluble in ferric sulphate solutions,¹ no loss of gold was detected after 34 days' contact with a tenth normal solution of that salt.²

In order to reproduce more nearly the conditions in nature experiment 5 was prepared as follows: a solution was made N/10 with respect to ferric sulphate and sulphuric acid, and N/25 with respect to sodium chloride. To 50 c.c. of solution 1 g. of powdered manganese dioxide was added and the experiment was carried on as before.³ The loss is comparable to that found in experiment 4,



allowing for the shorter time and the greater dilution of the chloride. The same experiment without MnO_2 showed no loss of gold.

After it had been shown that chlorides and manganese dioxide were necessary under these conditions, the next point to be determined was whether the free acid or the ferric chloride is the active agent in bringing about the solution. In experiment 6, 50 c.c. of N/10 HCl was used with 1 g. of powdered MnO_2 . In experiment 7, sodium hydroxide was added to 50 c.c. of N/10 ferric chloride solution until the precipitate formed barely redissolved on shaking,⁴ after which 1 g. of powdered MnO_2 was added.



¹ E.g., *Genesis of Ore Deposits*, 478, 481, and elsewhere.

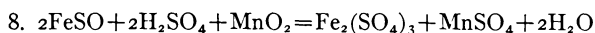
² This agrees with Stokes, *loc. cit.*

³ This is essentially the experiment of Rickard, *Trans. A.I.M.E.*, XXVI, 798. From experiments 6 and 7 it appears that the ferric salt is unnecessary.

⁴ Even then the solution was somewhat acid owing to the hydrolysis of the ferric chloride.

The experiments were conducted as before. The results show clearly that the free acid, rather than the ferric chloride, in the presence of manganese dioxide exercises the great solvent action, as the same amount of chlorine was present in both cases. Essentially, the most favorable conditions for the solution of gold are those in which free chlorine may be liberated.

W. J. McCaughey,¹ in studying the solubility of gold in ferric salt solutions, found that ferrous sulphate, even in very small amounts, had a marked effect in depressing the solubility of gold. Conceivably this may be a factor to be considered, and with this in view experiment 8 was performed, to determine whether ferrous sulphate, in the presence of sulphuric acid and manganese dioxide, would be quickly oxidized to the ferric salt, according to the following equation:



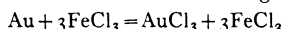
After acidifying 100 c.c. of 1.6 N. FeSO_4 solution with sulphuric acid, it was shaken vigorously with 5 g. of powdered MnO_2 . After five minutes the solution was filtered off. No ferrous iron was detected by the ferricyanide test, showing that the iron had been completely oxidized to the ferric state. The experiments were not done in such a way that the velocity of the oxidation could be measured, but the result shows that ferrous sulphate in acid solution is quickly oxidized by manganese dioxide, hence the suppression of the solution of gold by ferrous salts may be disregarded if manganese dioxide is present. It is interesting to note in this connection that the analysis of a sample of water from the Comstock Lode,² showing the greatest amount of ferric iron, showed a considerable amount of manganese, but no ferrous iron; a condition exactly in accord with the right-hand side of the above equation.

McCaughey's experiments on the solubility of gold in ferric salt solutions were made with stronger solutions than are known to occur in mine waters, but his results show that gold is attacked by ferric salts in the presence of hydrochloric acid.³ While no loss of gold

¹ McCaughey, *Jour. Am. Chem. Soc.*, XXXI, 1269.

² See analysis 3, p. 326. Nos. 5 and 6 illustrate the same fact.

³ If gold is dissolved by ferric chloride the reaction might be expected to be as follows:



This would seem to be a reversible action, as ferrous salts are commonly used as a pre-

was noted in experiment 3 as carried out by the writer, it is possible that in a longer time some loss might be detected, as more dilute solutions act more slowly.

SUMMARY

From the above experiments it appears:

1. That at the dilution of natural solutions of ferric salts their solvent effect on gold is probably very slight;
2. That in the presence of manganese dioxide no increased solubility is found unless chlorides are present;¹
3. That mixtures of ferric sulphate, sulphuric acid, and sodium chloride in concentrations common in mine waters will readily dissolve gold in the presence of manganese dioxide;
4. That free hydrochloric acid in the presence of manganese dioxide has a much greater solvent effect than the same amount of chlorine in ferric chloride solution;

cipitant for gold. McCaughey, however (*op. cit.*, footnote, p. 1270), failed to detect any ferrous salt after the action had gone on for two days. It seemed probable that ferrous chloride had been formed, but was oxidized by contact with the air. Accordingly the experiment was repeated in an atmosphere of carbon dioxide, care being taken to exclude, as far as possible, all contact with the air. Several possible sources of error were not eliminated and the experiment is only of preliminary nature. The results were as follows:

	LOSS OF GOLD	WEIGHT OF FERROUS IRON	
		Observed	Calculated
(a)...	0.02904	0.0240	0.02476
(b)...	0.03247	0.0282	0.02769

This seems to establish the correctness of the equation given above. The result is not in accord with the statement of McIlhiney (*Am. Jour. Sci.*, Ser. IV, II, 293) who found that gold dissolved in ferric chloride only in presence of air. The greater dilution at which he worked may account for this.

¹ The influence of manganese compounds in chemical reactions involving oxidation is noted in many cases. E.g., Moissan (*Chim. Minerale*, V, 617) states that fuming hydrochloric acid in presence of air will dissolve gold, especially if manganous chloride is present. The catalytic action of manganese dioxide in the decomposition of potassium chlorate and hydrogen peroxide are well known. Probably manganese compounds are of considerable importance in natural oxidations, even though they may be present in very small amounts.

5. That the influence of ferrous salts in suppressing the solubility of gold is negligible if manganese dioxide is present;

6. That the solution of gold is practically limited to the oxidized zone.

In agreement with these experiments is the fact that mangiferous lodes bearing pyrite, in areas of chloride waters, are leached to greater depths than lodes that do not carry manganese.¹

In conclusion, the writer wishes to thank Professor Emmons for his suggestions and advice in the conduct of the work, and Messrs. C. Russell and N. Sankowsky for placing at his disposal an unpublished tabulation of mine waters which they have assembled. Six complete analyses of vadose waters from their tables are appended:

	1*	2†	3‡	4§	5¶	6¶
Cl.	12.40	186.40	127.60	19.00	tr.	tr.
SO ₄	124.80	161.70	209100.00	474.00	258.40	26.55
CO ₃		1513.44		20.45		
NO ₃		1.60				
PO ₄		tr.				
K.		198.00		53.40		
Na.		719.45	535.00	132.00		
Li.		2.85				
Ca.	46.40	146.41	1286.00	100.100	121.40	72.48
Sr.		1.95				
Mg.	14.50	177.67	6590.00	5.88	13.08	14.90
Al.		1.06	9760.00	1.37	1.49	0.37
Mn.		0.57	885.10		4.72	4.12
Ni.					tr.	tr.
Co.					tr.	tr.
Cu.		0.02	147.50			
Zn.	8.90	0.34			2.82	47.40
Pb.		1.35				
SiO ₂	18.00	24.42	616.00	133.40	2.10	8.00
Fe++	} 6.60	} 3.50				
Fe+++			5025.00	6.33	4.74	6.30

* *U.S.G.S. Bull.* 330, 547.

† *Ibid.*

‡ *Bull. Univ. of Cal.*, IV, 192.

§ *Ibid.*, 189.

¶ Beck, *Nature of Ore Deposits* (Weed), II, 377. Analyses expressed in milligrams per liter. Where necessary they have been recast.

MARCH, 1910

¹ See W. H. Emmons, *Min. and Sci. Press*, December 11, 1909.